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FOUNDED BY JOHN D. ROCKEFELLER

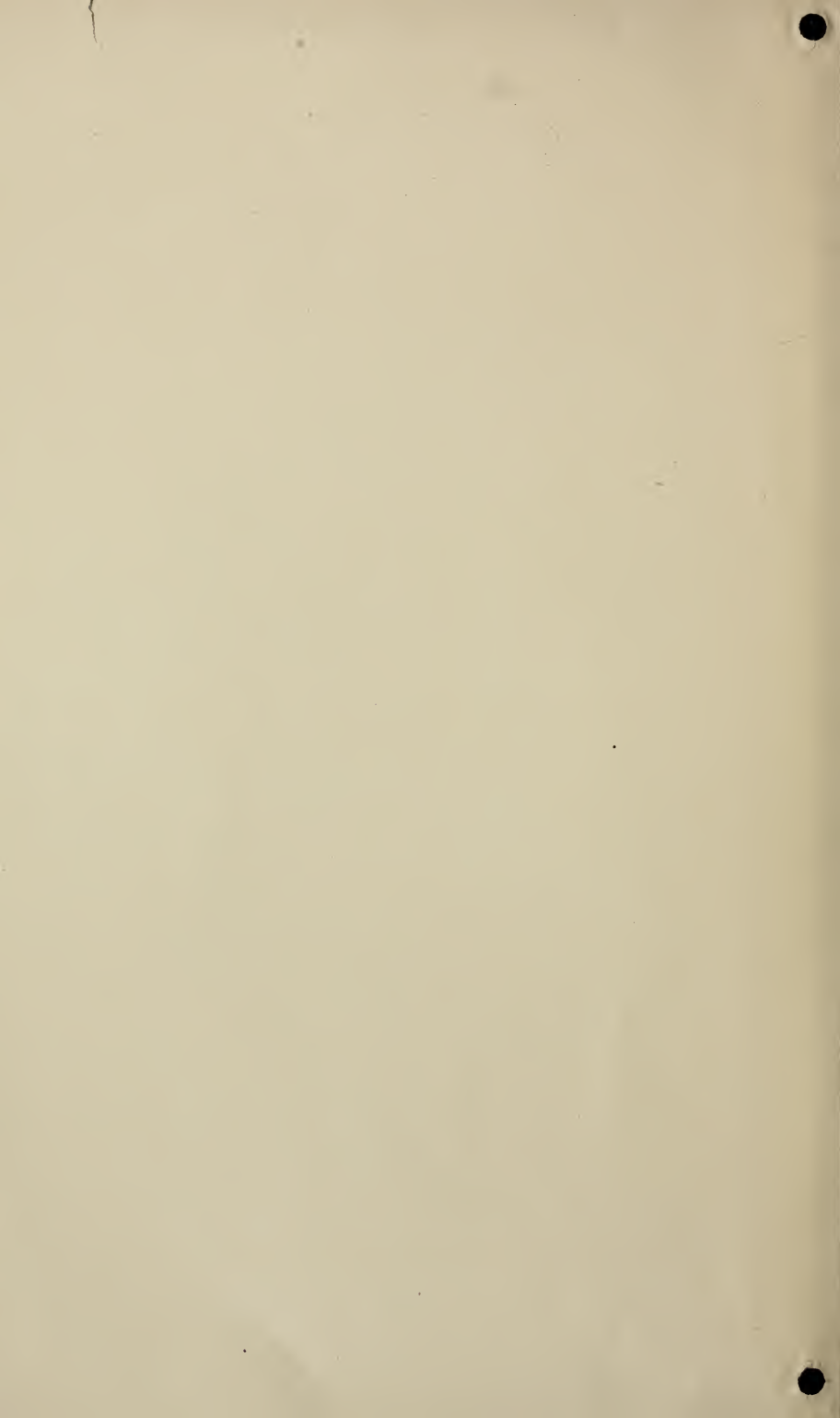# A NEW METHOD OF DETERMINING THE VAPOUR-DENSITY OF METALLIC VAPOURS

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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A new Method of determining the Vapour-Density of Metallic Vapours, and an Experimental Application to the Cases of Sodium and Mercury. *By* FRANK B. JEWETT.

IN all investigations on the composition and distribution of light in the spectral lines it is of prime importance that the lines themselves be as narrow and sharply defined as possible ; this is especially true in those cases where the analysis is carried on by means of interference phenomena, for here the difference of path over which interference takes place decreases as the width of the line increases.

There are in general two causes which may affect the breadth of the lines : (*a*) motion of the light-producing molecules in the line of sight, and (*b*) change in the period of the source caused by frequent collisions of the molecules [*]. To these might be added a third cause, suggested by Lommel [†], in which an inhomogeneity is produced in the source by forced changes in the period of ionic vibration, thus putting an upper limit on the power to produce interference-fringes ; this latter supposition is, however, yet to be verified, and from the present experimental data it seems probable that any

[*] Michelson, Phil. Mag. (5) xxxiv. p. 293.
[†] Lommel, Wied. *Ann.* iii. p. 251 ; Drude, *Lehrbuch der Optik*, p. 498.
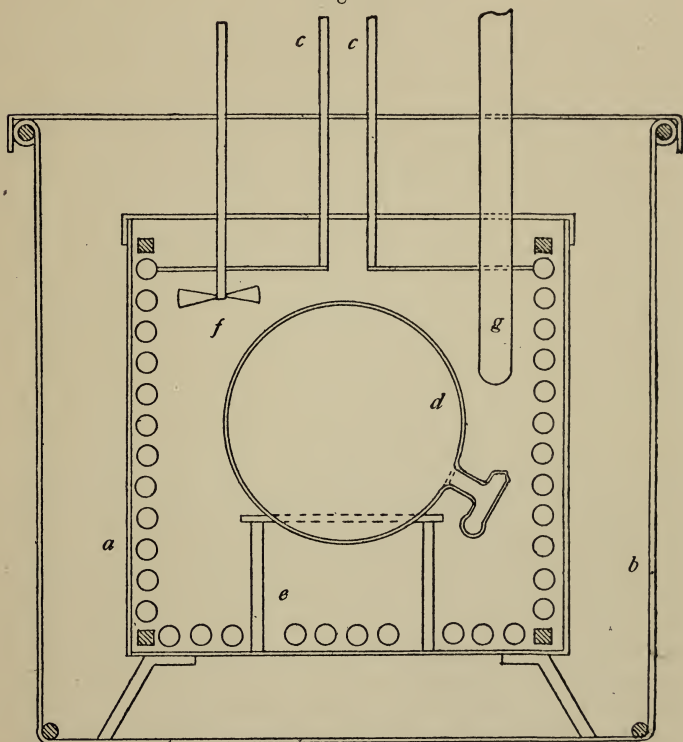
effect due to it must be almost if not wholly negligible in comparison with that of (*a*) and (*b*). This being the case, the determination of the relative importance of the two factors, pressure and temperature, is the question which at once presents itself for solution. In his very exhaustive article on "The Application of Interference Methods to Spectroscopic Measurements" Professor Michelson has taken up this problem in considerable detail. He finds that in the cases where the density of the vapour is very low the effect of changing pressure on the width of the spectral lines is almost wholly negligible ; for hydrogen this is true even in the case where the pressure is as high as 2 or 3 mm.; in fact, when the relation between the breadth of the lines and 1/P (pressure) is plotted the influence of P is seen to become vanishingly small at about 5 mm. In summing up, Professor Michelson states as follows :—" It thus appears that in the case of hydrogen—and probably in all other cases—the width of the spectral line diminishes toward a limit as the pressure diminishes, which limit depends upon the substance and its temperature ; and that the excess of width over this limit is simply proportional to the pressure."

As mercury and sodium are both readily usable in vacuum-tubes, the foregoing facts would suggest them at once as the ideal substances for an experiment on the effect of pressure and temperature on the broadening of the spectral lines. As a preliminary to such an experiment a knowledge of the densities of the saturated vapours at various temperatures is of course necessary. In addition to making a determination of the densities for such a purpose as the above, there is still another and even more urgent reason, viz., the evident dependence of the change in the lines in the Zeeman effect, and also in some cases the reversal of the same, upon the density of the light-producing vapour. It was particularly with a view to the solution of this latter problem that the following experiment was proposed and undertaken.

Apparatus.—The method employed was one suggested by Prof. Michelson, in which the amount of vapour filling a known volume is determined by finding the amount of condensed metal in the observing flask when the latter is cooled off. The apparatus consisted of three essential parts—the heating-bath, the gas-bulb, and the thermometer. The bath finally found most satisfactory is shown in section in fig. 1 (p. 548); *a* and *b* are two sheet-iron boxes lined inside and out with heavy sheet-asbestos, and having a 3-inch air-space between them ; the inner box (*a*) is about 14 inches on a side ; around the inside and on the bottom of *a* are a number of iron

resistance-coils carried on an asbestos-covered iron frame, and ending in two heavy terminal wires *cc*, which pass out
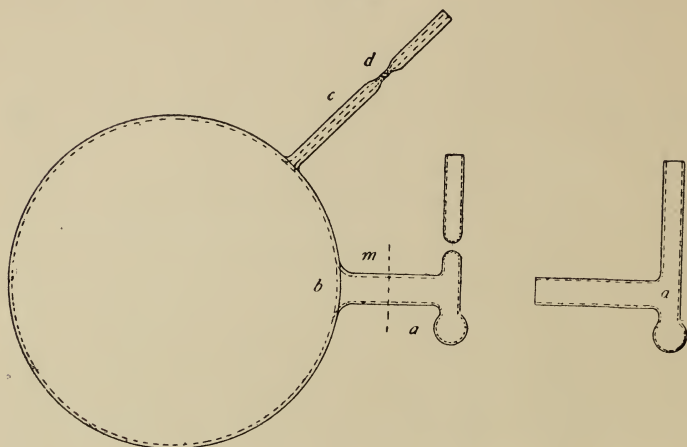
Fig. 1.

through the covers of both boxes ; the bulb *d* is supported on a metal frame *e*, and constant circulation is maintained by an electrically-driven fan *f* ; *g* represents the stem of a platinum thermometer. With this arrangement, and with suitable regulation for the current, the temperature may easily be kept constant at any desired point to within one or two degrees *.

The gas-bulb or reservoir (fig. 2) was of hard glass of known cubical content, and had a capacity of about 2000 c.c. ; proceeding from the bulb were two tubes, one a heavy capillary and the other with an internal diameter of about 1 cm.

* In one instance where the bath was used for calibrating a Beckmann thermometer the temperature was held constant to 0°·1 for fifteen minutes.

The thermometer was of the Callendar platinum-resistance type [*], with auxiliary compensating-leads and direct reading

Fig. 2.

Wheatstone bridge, and was capable of reading to $0°·005$; this particular instrument was one of those calibrated at the Kew Observatory.

In order to make an observation a tube (a, fig. 2) was sealed to the larger tube (b), and the capillary-tube (c) drawn down at (d); this being done, and both tubes and bulb thoroughly dried, a small piece ($0·5$–$0·7$ gm.) of C.P. metallic sodium was introduced into (a), and the latter quickly sealed off at (e), as shown; (c) was now connected to a Geissler-pump, and the air drawn out to a residual pressure of $0·1$–$0·2$ mm., after which the bulb was filled with some inert gas (H or N) and again pumped out and the capillary-tube sealed off at (d). The bulb thus prepared was now introduced into the bath and the temperature raised to any required point; the apparatus was kept at the desired temperature for fifteen or twenty minutes, thermometer-readings being taken every two minutes; the cooling had to be done very slowly, as the capsule containing the molten sodium was very liable to crack, and the inrushing air carried the metal into the bulb. Upon removing the latter from the bath, the whole inner surface showed a bright metallic coating of condensed sodium vapour, varying in thickness with the temperature to which the bulb had been subjected. To determine the amount of

[*] E. H. Griffiths, 'Nature,' Nov. 14, 1895.

so lium in this coating, and consequently the amount of saturated vapour that had filled the bulb, the tube (*b*) was cracked off at some point (*m*), thus getting rid of the metal remaining in (*a*); the bulb was then thoroughly washed out with hot water until the washings failed to show an alkaline reaction with phenolphthaline, and the amount of Na present as NaOH in the washings determined by differential titration with standardized $N/10 \cdot NaOH$ and $N/10 \cdot H_2SO_4$ solutions; this amount, together with the corrected volume of the bulb, furnished the requisite data for finding the vapour-density. As this process had to be repeated for every determination, the making of a large number of observations was an exceedingly tedious matter.

The above-described method was the one finally chosen for sodium; a number of methods depending upon the gravimetric determination of the amount of metal volatilized, while giving good results for those metals which do not oxidize easily at low temperatures, *e. g.* Cd, proved absolutely useless in the case of sodium on account of the rapid oxidization of the latter when in contact with the air.

A difficulty which it was at first feared might render the determination impossible at the higher temperatures, viz., the action of sodium on glass, was not encountered except when the residual atmosphere contained O or water-vapour, the solvent action being apparently exhibited only for the oxide or hydroxide; aside from this fact the results obtained in the presence of air were so extremely erratic that all the final determinations were made either in the presence of oxygen or nitrogen. (The majority of the tests were made with hydrogen, and as they gave consistent results the accuracy of the process was not questioned at the time, especially as the hydride, Na_4H_2, was not supposed to form at pressures so reduced as those employed [*]. Owing, however, to a peculiar brown metallic appearance of the deposit in some instances, doubt was cast on the validity of this assumption, so that while the great mass of chemical data seems to weigh against the formation of the hydride, there still remains the possibility that the density of the vapour, calculated on the assumption that it consisted of free Na, gave too low a result. This question can be easily settled, however, by the employment of N, since the nitride, NaN_3, is not formed by the direct combination of Na and N [†].)

Some of the results are given in Table I., and the curve,

[*] Roscoe & Schorlemmer, ' Treatise on Chemistry,' vol. ii. pt. i. p. 107.
[†] *Berichte*, xxv. p. 2084 (1892); *Zeit. f. anorg. Ch.* vi. p. 38 (1894).

with temperatures as ordinates and densities as abscissæ, is shown in fig. 3 (p. 552); the dotted curve shown is that for Hg at temperatures where the density of the vapour corresponds to that of Na ; the temperatures for this latter curve are indicated on the curve.

TABLE I.

Temp.	Density.
$^{\circ}$ 368	0 00000009
373	0·0000002
376	0·00000035
380	0·00000043
385	0·00000103
387	0·00000135
390	0·00000160
395	0·00000270
400	0 00000350
406	0·00000480
408	0·00000543
412	0·00000590
418	0·00000714
420	0·00000750

While the densities were not obtained much below 365°, it will be noticed that at this temperature—which cannot be far from that commonly employed in vacuum-tube work *— the density of the Na vapour increases at about the same rate as that of Hg at 85°, while at points slightly above this the Na curve increases much the more rapidly. This fact, taken together with its low atomic weight, might well account for the peculiarities observed by Professor Michelson.

As was stated above, the experiment was undertaken solely to determine the densities within the range between 350° and 450°, and indeed the use of a glass bulb precludes the possibility of anything being done above 500°; with a porcelain bulb it would be comparatively easy to attain any desired temperature below 1700°.

The ease with which the temperature of the electric bath could be regulated at once suggested the desirability of making a series of determinations on the vapour-density of Hg, and with the slight alteration in the form of the bulb

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* Professor Michelson assumes that the temperature of the heating-box, 350°, is that of the vapour also. There appears to be some doubt as to the legitimacy of this assumption, owing to the very considerable heating produced by the discharge itself.
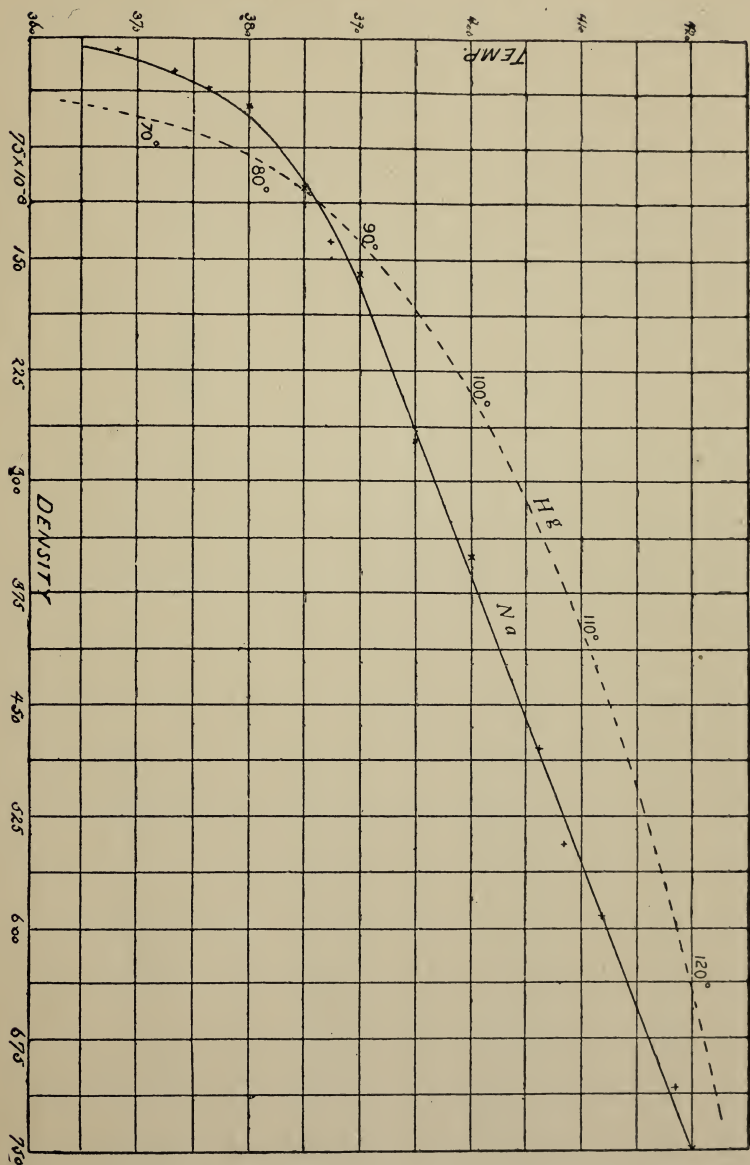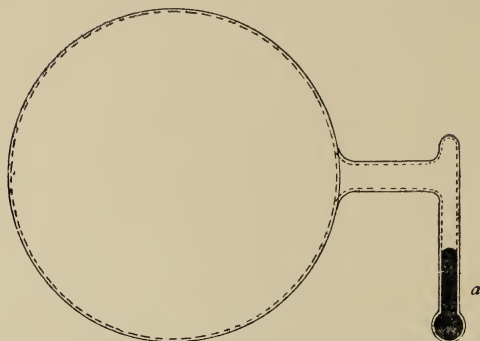
Fig. 3.

shown in fig. 4, a set of continuous readings 5° apart was
obtained. The mercury-reservoir (*a*, fig. 4) is a long narrow

Fig. 4.

tube of hard glass of known coefficient of expansion, and
having a carefully calibrated bore. In making a deter-
mination the reservoir is charged with a known weight of
mercury, and the bulb exhausted and sealed off as in the case
of sodium ; it is then introduced into the bath and supported
in such a position that (*a*) is vertical ; the height of the
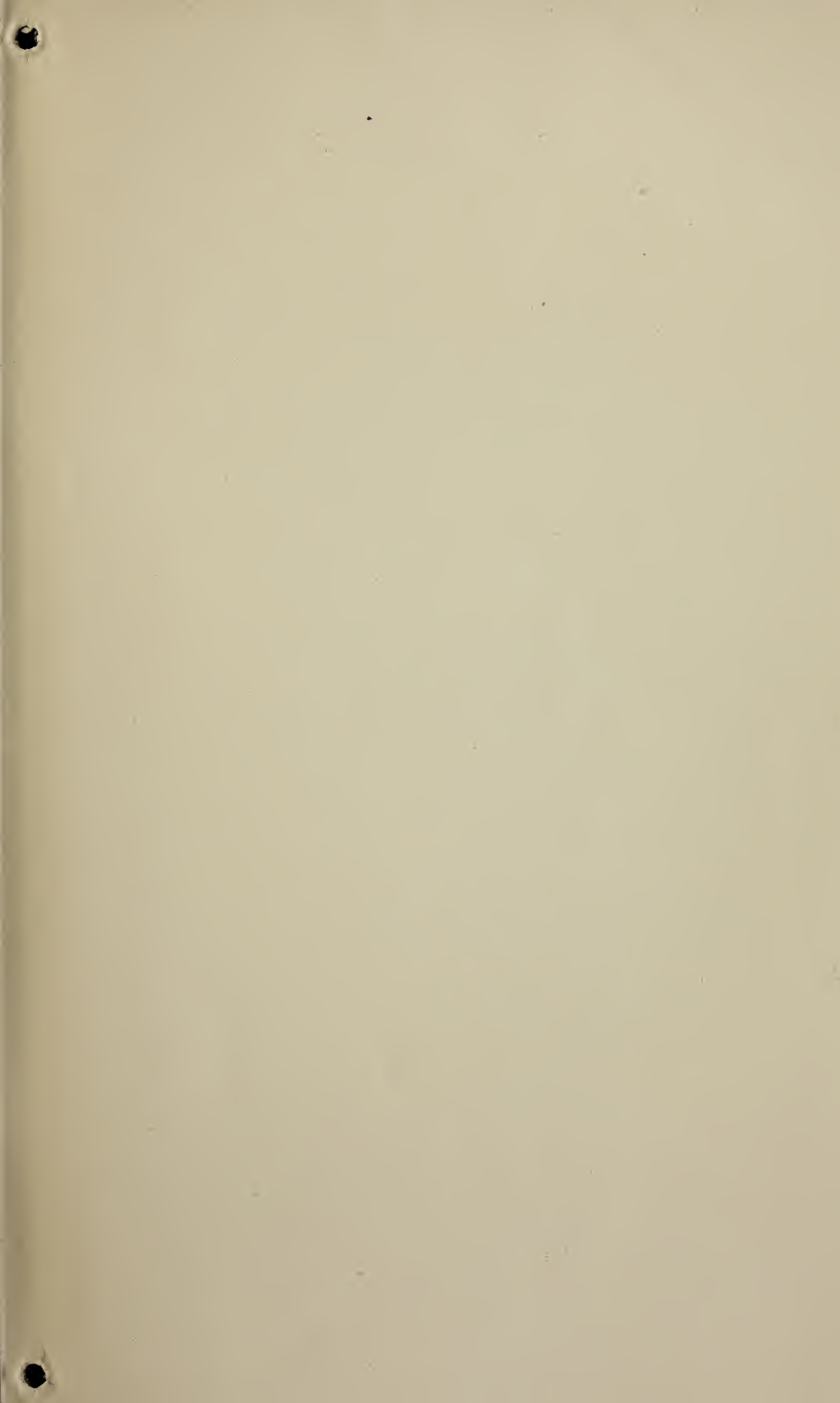mercury column is observed through glass windows in the

TABLE II.

Temp.	Density.	Regnault & Hertz.	Ramsay & Young.
40	0·00000007	0·00000007	0·00000009
60	0·0000003	0·0000003	0·0000003
70	0·00000045	0·0000005	0·0000005
80	0·0000007	0·0000008	0·0000008
90	0·0000012	0·0000014	0·0000014
100	0·0000021	0·0000024	0·0000023
110	0 0000040	0·0000039	......
120	0·0000060	0·0000064	0·0000059
140	0·0000138	0·0000147	0 0000137
160	0·0000302	0·0000323	0·0000297
180	0·0000624	0·0000649	0·0000603
200	0·0001580	0·0001236	0·0001152
220	0·0002020	0·0002271	0·0002077
240	0·0003754	0·0003673	... ..
260	0·0005830	0 0005817	......
270	0·0006528	0·0007257	0·0007310
280	0·0008645	0·0008994	0·0009113
300	0·0013466	0·0013547	0·0013796
305	0·0013882	......	......
310	0·0016447	0·0016472	0·0016734
320	0·0019879	0·0019921	0·0020180
325	0·0019960	......	......

sides of the bath by means of a cathetometer. The readings thus obtained, together with the known coefficients of expansion of glass and mercury, furnish the requisite data for determining the amount of metal volatilized. A partial series of the results obtained is given in Table II., together with the results calculated from the observed tensions of mercury-vapour as given by Regnault and Hertz; a more complete set of readings will be published later.

In conclusion I desire to express my thanks to Professor Michelson for the encouragement and helpful criticism given throughout the work, and also to Dr. Gale for the assistance so kindly rendered in the work on the density of mercury-vapour.

Ryerson Physical Laboratory,
    March 25, 1902.